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2-D Polymerized Langmuir-Blodgett Films Studied by STM

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2-D Polymerized Langmuir-Blodgett Films Studied by STM

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Abstract

The monomer 3-hexadecyl pyrrole was polymerized at the gas/liquid interface. Monomer and polymer were transferred from the interface to MoS₂ for investigation by STM after annealing. Monolayers of monomer and polymer were highly ordered showing orientational and positional correlation of alkyl side chains. Polymer monolayers showed increased side chain packing density and side chain orientation more orthogonal to the surface. Polymer multilayers showed disorder, revealing connectivity and curvature of polymer chains. Conformations of polymer chains suggest growth occurs in a parallel fashion at the gas/liquid interface.

Two-dimensional (2-D) polymer monolayers can be formed by reacting monomer deposited on a solid surface or confined to a gas/liquid interface^{1,2}. Restricting monomer molecules to a planar surface during polymerization prohibits the resulting polymer chains from overlapping. An important difference between the above two reaction environments and a distinct advantage of interfacial reactions is that constant intermolecular distances can be maintained through applied surface pressures. Thus, unlike reactions at solid surfaces where monomer is topologically confined, conversion is not limited due to lateral shrinkage. Although orientation at the aqueous surface reduces the number of conformations the chains can assume, many possibilities exist because of the monolayer fluidity. Figure 1 pictorially shows several likely conformations. It has been argued that insolubility of an isolated growing polymer chain in monomer should result in a conformation minimizing contact between the two phases³ (Figure 1a). However, no experimental data has been reported to confirm this argument. Other possibilities may include lamellar-type growth, analogous to chain folding observed in semi-crystalline materials such as polyethylene⁴ (Figure 1b), or parallel chain growth, initiated by alignment of oligomer molecules during the reaction. Although many types of 2-D polymerizations at gas/liquid interfaces (Langmuir polymerizations) have been reported, no experimental data exists describing the conformation of the resulting polymer chains.

By introducing a conducting polymer backbone we report on scanning tunneling microscopy (STM) investigations of Langmuir polymerized monolayers. Our goal is to elucidate the main chain conformation and compare results with the above models. Poly (3-hexadecyl pyrrole) and its monomer (Figure 2) were used for these investigations as they both form stable monolayers at the aqueous interface and can be transferred to solid substrates^{5,6}. We will compare the ordering observed in monolayers of monomer and polymer, and polymer

multilayers, all which were transferred to molybdenum disulfide (MoS_2) substrates and then annealed. MoS_2 was used as a substrate because of the high degree of freedom allowed for molecular alignment⁷. It also provides good STM contrast conditions for molecules containing alkyl chains and is molecularly smooth without dangling bonds. The Langmuir trough was used to establish constant average intermolecular distances, quasi two dimensionality during polymerization, and uniform film thickness; not to define local lateral order in the transferred films. Samples were thermally annealed above their bulk melting points prior to STM imaging.

STM has been utilized to investigate packing in transferred Langmuir Blodgett (LB) monolayers⁸ and low molecular weight adsorbates on solid substrates, though limited molecular information has been obtained for LB films. This limited information has been attributed to the poor conductivity of the LB layer, a direct consequence of molecular packing orthogonal to the substrate plane. As a result, Atomic Force Microscopy has been more commonly used to image LB films^{9,10}. In our case, the intrinsic conductivity of the polypyrrole backbone should change the contrast and allow us to image both monolayers and multilayers by STM more successfully than conventional LB materials.

Figure 1d describes the experimental details of the Langmuir polymerization. All monolayer samples were prepared by one upstroke of the MoS_2 substrate, placing the hydrophilic pyrrole rings or the polypyrrole backbone at the MoS_2 surface. Multilayer samples were prepared by alternating up and down strokes through the interface.

An STM image of a monolayer of 3-hexadecyl pyrrole monomer is presented in Figure 2a. Clearly distinguishable rod-like structures, corresponding to individual molecules, display both orientational and positional correlation; that is, each molecule is oriented perpendicular to the scanning direction and positioned

into regular, interdigitated rows. Measurement of the molecules suggests they are arranged with the pyrrole ring oriented in the plane perpendicular to the substrate surface. Another important feature is the nearly parallel alignment of the molecule's longest axis to the substrate surface. The significance of this observation is two-fold. First, similar alignment is a characteristic feature observed in STM images of rod-like molecules after annealing¹¹. Second, the surface density of the molecules must decrease during the annealing process for molecules to "lie flat". Specifically, some of the molecules in the pre-annealed LB layer must have been extruded from the surface during annealing. Apparent "sweeping" of excess material by the STM tip and formation of large granules on the surface as samples age, suggest this process does indeed occur.

An STM image of a poly (3-hexadecyl pyrrole) monolayer is presented in Figure 2b. Like the monomer, similar rod-like structures displaying orientational alignment perpendicular to the scanning direction are observed. In contrast, however, a different length and periodicity are observed in two directions of positional row alignment. Each rod-like structure may correspond to a single alkyl side chain along the polymer backbone, but clearly the backbone is not visible. This is due to placement of the polymer backbone at the substrate surface during the transfer process and the high packing density of the alkyl side chains which orient away from the substrate. Comparison with the monomer image indicates that the side chain packing density in the polymer monolayer is indeed greater. The increased side chain density is related with two structural distances. The first is the chemically defined repeat distance determined by the chemical bonds and configuration of the underlying polymer backbone. The second involves the proximity of one polymer chain to another. The alkyl side chain ordering observed in the polymer image can be explained by an all anti conformation of the polypyrrole backbone with respect to the nitrogen, such that each polymer chain

arranges its alkyl side chains into two parallel rows. In this conformation the distance between these two parallel rows of alkyl side chains corresponds to nearly twice the MoS₂ lattice spacing. Polymer main chains are then aligned in a parallel fashion suggestive of the overall conformation depicted in Figure 1c. If the distance between the polymer main chains is also twice the MoS₂ lattice spacing, this conformation accurately explains the uniform structure and the two directions of row alignment observed in the STM images. The very uniform structure indicates that molecule-MoS₂ interactions play an important role in defining surface order and in determining distances between polymer chains. Similar phenomena have been observed for systems of low molecular weight rod-like molecules¹².

Both monomer and polymer required annealing to obtain very high molecular resolution by STM, again emphasizing the importance of molecule-substrate interactions in defining surface order. The degree which annealing affected the two systems, however, was very different. The monomer was easily reordered from its original packing in the LB layer by extrusion of some molecules from the surface. In the case of the polymer, respacing and realignment of the polypyrrole backbone with a major axis of the MoS₂ occurred, but overall the layer showed a greater stability associated with higher molecular weight molecules.

Figure 3a-d shows STM images of a polymer multilayer. Again, rod-like structures are seen corresponding to the alkyl side chains. In contrast to the polymer monolayer, however, the alkyl side chains no longer show very high orientational correlation. More specifically, the side chains do not uniformly orient perpendicular to the scanning direction and display a general increase in disorder. This disorder, however, now reveals evidence of connectivity between the alkyl side chains. Each polymer chain still shows positional row correlation but the chains now appear to "drape" themselves over defects in the layers below and to

show curvature in the layer plane. Inter-row distances also show local variations not observed in the monolayer images.

The multilayer polymer images are clearly more disordered than the monolayer images of Figure 2. The wavy structures suggest we are not "imaging through" the overlayers and observing the layer adjacent to the substrate surface. Were this the case, then significantly more row order would be present. Therefore the disorder is related to the absence of molecule-substrate interactions and the polymer overlayers exhibit conformations less restricted than those topologically confined by a highly ordered substrate surface.

There are clear similarities and important differences between all the above images. Both monolayer images show very ordered structures with both orientational and positional correlation. The annealing process allows monomer molecules to orient parallel to the surface. In the case of the polymer, annealing allows the polymer backbone to become aligned parallel with a major axis of the MoS₂ substrate and establishes positional order. Thus both the positional order and chemical repeat distance define the side chain packing density. As a result, the side chains do not align parallel to the substrate as in the monomer monolayers; instead they remain partially erect due to steric interactions with adjacent side chains.

In the case of the polymer multilayer, the backbone in the outer layer is not orientationally ordered by the MoS₂. This allows it to take up conformations more akin to those intrinsic to the polymerization process at the gas/liquid interface. Moreover, either the molecular conformation or contrast conditions allow greater evidence of the connectivity related to the backbone to be observed. As a result, the conformation of the first layer appears to be highly dependent on the molecule-substrate interactions, while that of subsequent layers shows increasing disorder. This is shown pictorially in Figure 4. The above observations lead us to believe

that the outermost layer is most reminiscent of that resulting from parallel growth of polymer chains (Figure 1c). Both spiral-type conformations and 2-D chain-folded lamella are not supported by our observations. It appears that the fluidity of the monolayer surface plays an important role in the resulting polymer chain conformation. The tendency for a polymer chain to phase separate as a single unit or to fold back and forth across itself must compete with nematic-like domain formation by small oligomer molecules¹³. The former two conformation possibilities require a greater degree of polymerization to become dominant. On a fluid surface such as a gas/liquid interface, rapid domain formation by small oligomer molecules is possible and would likely favor conformations dominated by parallel alignment of the polymer chains. Thus, the fluidity of the gas/liquid interface may amplify the rate dependence of the resulting polymer conformations compared to those observed at a solid surface.

Another important result of these investigations was that the introduction of a conductive polymer backbone did result in successful imaging of both LB monolayers and multilayers. As such, these highly ordered polymer monolayers may provide a new class of adsorbates to flexibly modify MoS₂ and other substrates. Thus, using conductive polymer films as underlayers to change lattice spacing or contrast conditions may prove useful for studying other systems such as alignment in liquid crystals or functional group effects in molecule-molecule interactions.

Figure Captions

Figure 1. Parts 1a-c pictorially show a bird's eye view of several likely polymer conformations at the gas/liquid interface, monomer molecules are represented by unfilled circles while polymer chains are depicted by connected, filled circles. (a) spiraling, single chain phase separation, (b) lamellar-type chain folding, and (c) parallel chain alignment; Part d gives experimental details of the Langmuir polymerization of 3-hexadecyl pyrrole. By spreading monomer at room temperature on an oxidizing subphase (0.03 M ammonium persulfate) and compressing to form a dense packed monolayer, polymerization of 3-hexadecyl pyrrole monomer can be performed. Barrier displacement is used to maintain constant applied surface pressure (10 mN/m) and compensate for lateral shrinkage during the polymerization. The progress of the polymerization reaction can then be monitored by observing subsequent changes in surface area. The reaction is complete when the average barrier speed decreases to zero and the mean molecular area becomes constant. Molecular weights as measured by size exclusion chromatography with polystyrene standards are typically 3500-6000.

Figure 2. STM images of monomer and polymer monolayers measured by a Nanoscope 2® instrument (all images taken in constant current mode in air). (a) 3-hexadecyl pyrrole monomer; dimensions: 10 nm by 10 nm, tip bias voltage: -1320.5 mV, current: 0.31 nA (b) poly(3-hexadecyl pyrrole); dimensions: 10 nm by 10 nm, tip bias voltage: 1400.2 mV, tunneling current: 0.20 nA. Insets show chemical structures of

monomer and polymer. STM samples were prepared by vertical transfer of preformed monolayers to MoS₂ substrates. All monolayers of 3-hexadecyl pyrrole monomer were transferred at 10 mN/m from a pure water (>18 M Ω) subphase. Polymer monolayers were transferred at 20 mN/m directly from the oxidizing subphase used for the polymerization reaction. All transfers were performed under isobaric conditions and samples annealed above their bulk melting points for at least 12 hours. Samples were cooled to room temperature at a rate of 5 °C every 15 minutes before being imaged by STM.

Figure 3. STM images of polymer multilayers. (a-f) poly(3-hexadecyl pyrrole); All image dimensions: 11.8 nm by 11.8 nm, tip bias voltages (all): 1980.6 mV, tunneling currents ranged from: 0.13 - 0.14 nA. The sample was prepared from a mixed monolayer containing 64% of the low molecular weight liquid crystal 8CB, used as a processing aid and to establish additional disorder at the surface. Note the polymerization was carried out prior to the addition of 8CB. The samples were prepared by vertical deposition at an applied pressure of 8 mN/m and were nominally 3 layers thick. The sample was annealed after transfer of all layers as indicated in Figure 2.

Figure 4. Pictorial model of the multilayer structure observed. The innermost layer against the MoS₂ surface is likely to be highly ordered with the polymer backbone oriented directly against the substrate surface. Subsequent overlayers are much more disordered, and more closely reflect the polymer backbone conformation after polymerization at the gas/liquid interface.

Figure 1 -- Parts a, b, c

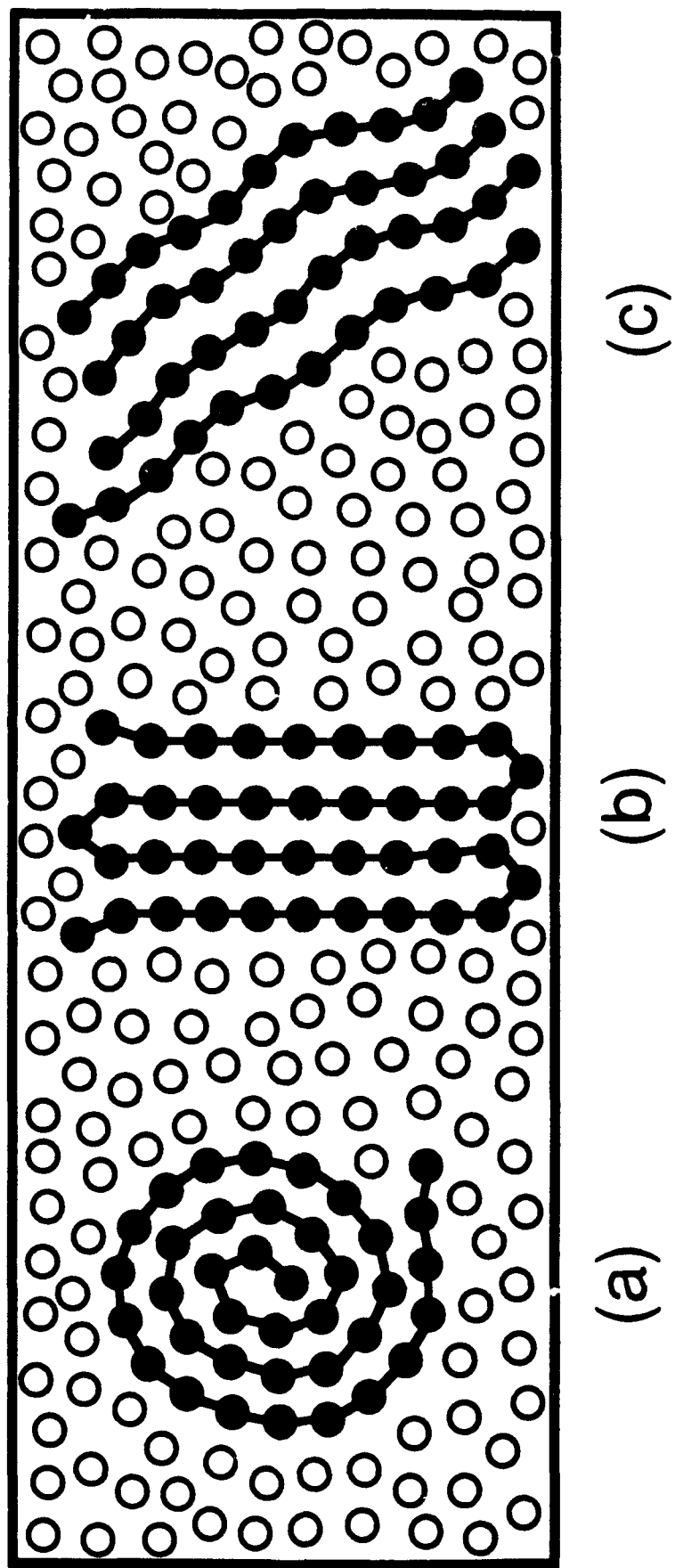


Figure 1 -- Part d

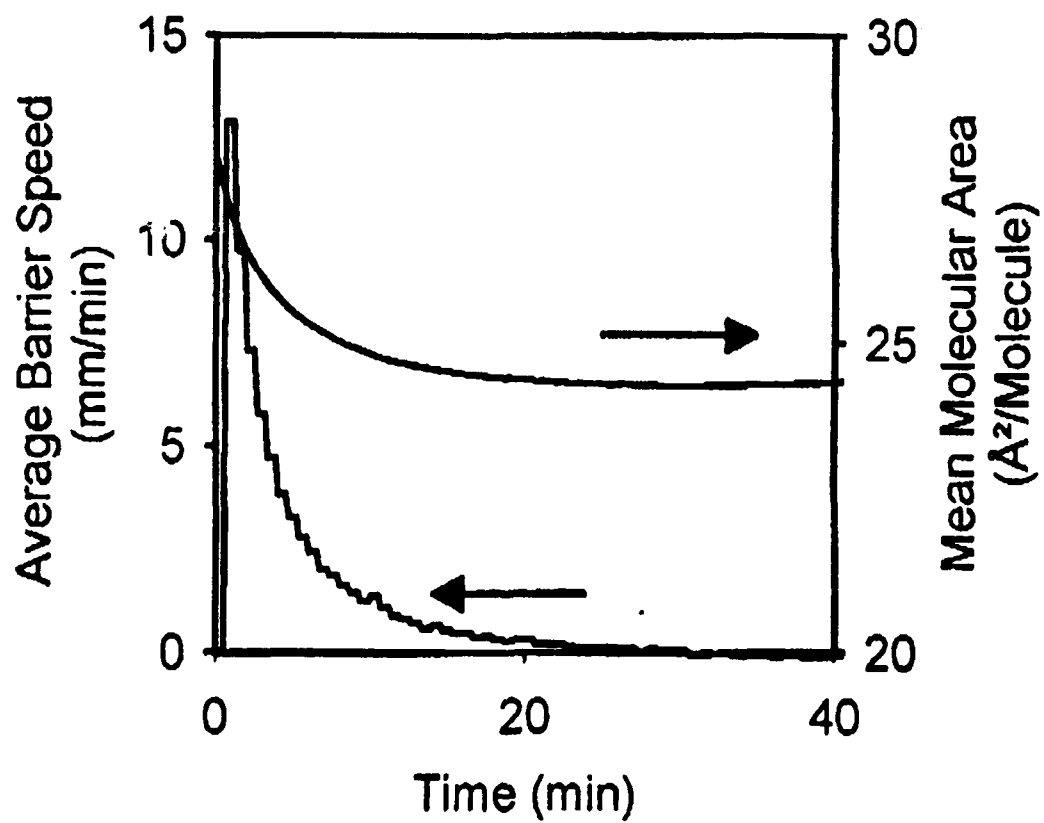
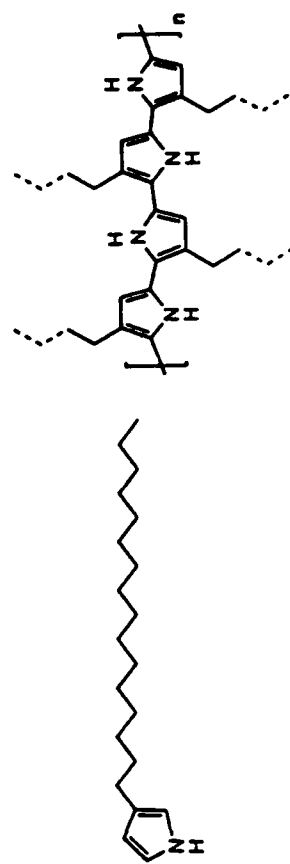
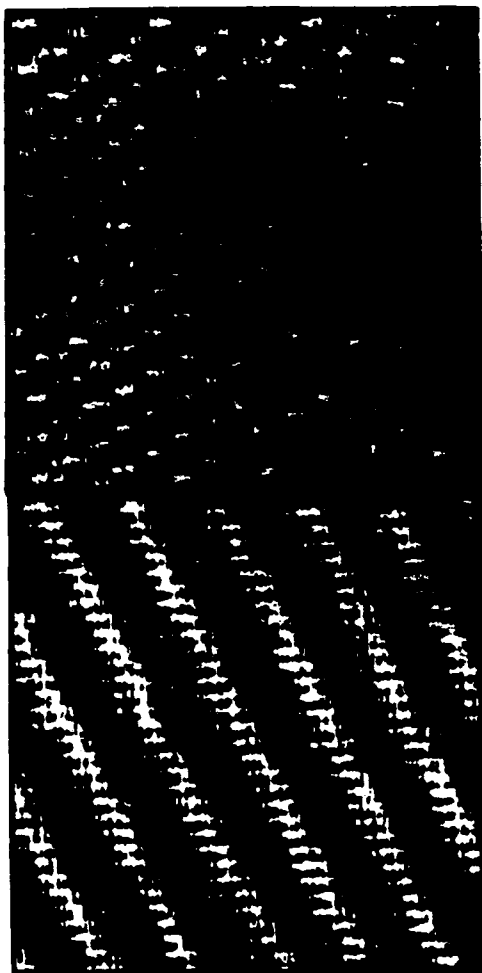


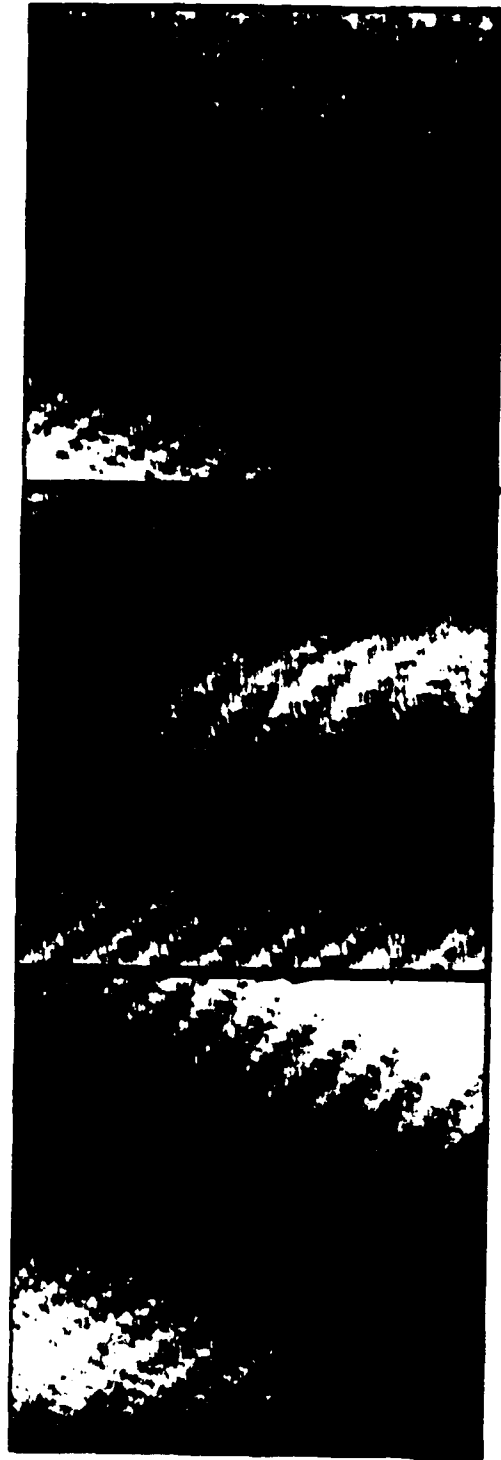
Figure 2 -- Parts a, b



(a)

(b)

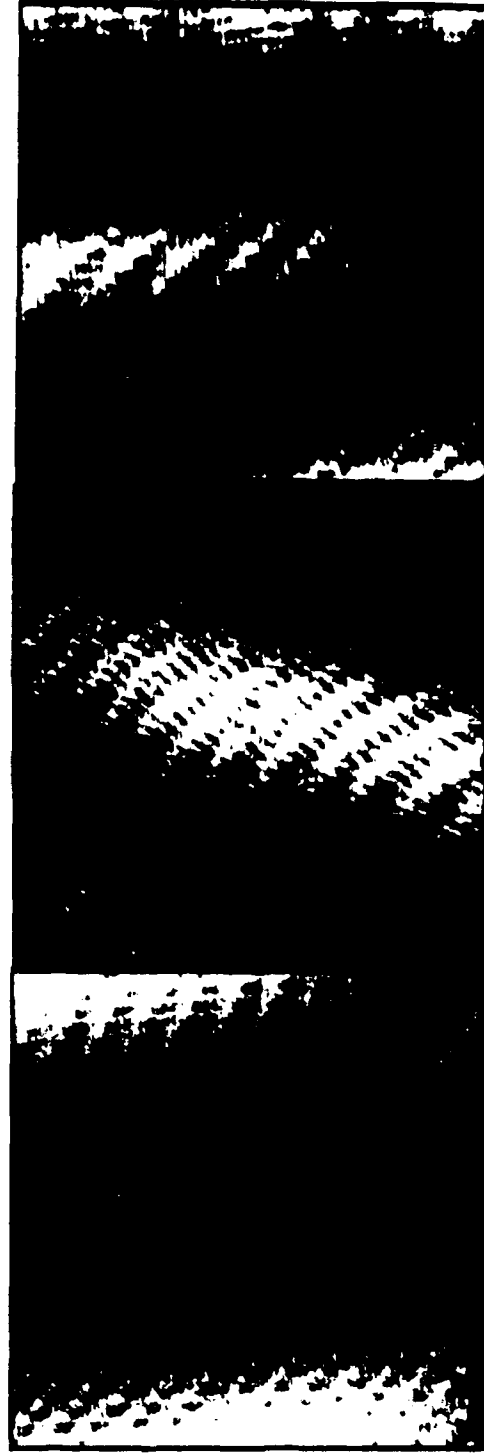
Figure 3 -- Parts a, b, c, d, e, f



(a)

(b)

(c)

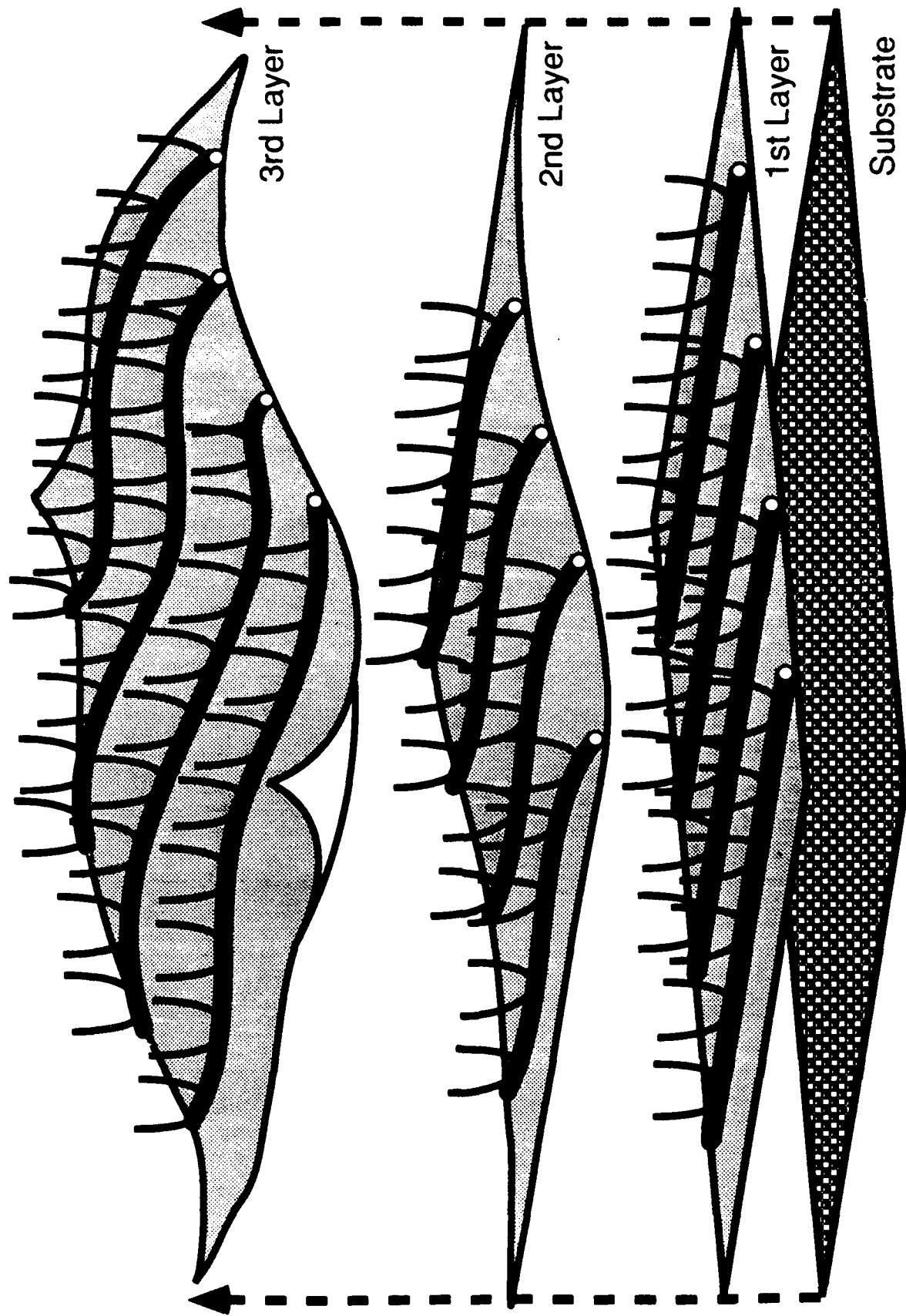


(d)

(e)

(f)

Figure 4



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